and its properties render it probable that it will be found to be isomeric with the product of decomposition previously mentioned. I am engaged in a more minute examination of this compound, which I hope may assist in explaining the cause of the still enigmatical isomerism exhibited by the derivatives of phenylamine.

I have already repeatedly called attention to the different atomicity exhibited by nitrogen under different conditions. In the derivatives of amidobenzoic and of anthranilic acids, it can be proved that 1 equiv. of nitrogen replaces 1 equiv. of hydrogen; while in the derivatives of phenylamine, the nitrogen is present with the value of three molecules of hydrogen.

The experiments which I have described were performed in Dr. Hofmann's laboratory.

IX. "Contributions towards the History of the Monamines."—No. III. Compound Ammonias by Inverse Substitution. By A. W. Hofmann, LL.D., F.R.S., &c. Received July 24, 1860.

Many years ago I showed that the bromide or iodide of a quartary ammonium splits under the influence of heat into the bromide or iodide of an alcohol-radical on the one hand, and a tertiary monamine on the other.

Having lately returned to the study of this class of substances, I was led to examine the deportment, under the influence of heat, of the tertiary, secondary, and, lastly, of the primary monammonium-salts.

Experiment has shown that these substances undergo an analogous decomposition. The chloride of a tertiary monammonium when submitted to distillation yields, together with the chloride of an alcohol-radical, a secondary monamine; the chloride of a secondary monammonium, together with an alcohol-chloride, a primary monamine; lastly, the chloride of a primary monammonium, the chloride of an alcohol-radical and ammonia.

Exactly, then, as my former experiments show that we may rise in the scale by replacing the four equivalents of hydrogen in ammonium one by one by radicals, so it is obvious from these new experiments

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to *Proceedings of the Royal Society of London.* www.jstor.org

that we may also step by step descend, by substituting again hydrogen for the radicals in succession.

To take as an illustration the monammonium-salts of the ethyl-series which as yet I have chiefly examined :

Ascent.

$$\underbrace{H_3\,N}_{\text{Ammonia.}} + \underbrace{(C_2\,H_5)\,Br}_{\text{Bromide of ethyl.}} = \underbrace{[(C_2\,H_5)\ H_3\,N]\,Br}_{\text{Bromide of Ethylammonium.}}$$

$$\underbrace{(C_2\,H_5)\ H_2\,N}_{\text{Ethylamine.}} + (C_2\,H_5)\,Br = \underbrace{[(C_2\,H_5)_2\,H_2\,N]\,Br}_{\text{Bromide of Diethylammonium.}}$$

$$\underbrace{(C_2\,H_5)_2\,H\ N}_{\text{Diethylamine.}} + (C_2\,H_5)\,Br = \underbrace{[(C_2\,H_5)_3\,H\ N]\,Br}_{\text{Bromide of Triethylammonium.}}$$

$$\underbrace{(C_2\,H_5)_3\quad N}_{\text{Triethylamine.}} + (C_2\,H_5)\,Br = \underbrace{[(C_2\,H_5)_4\quad N]\,Br}_{\text{Bromide of Tetrethylammonium.}}$$

Note.—$H=1$; $C=12$.

Descent.

$$\underbrace{[(C_2\,H_5)_4\quad N]\,Cl}_{\text{Chloride of Tetrethylammonium.}} = \underbrace{(C_2\,H_5)\,Cl}_{\text{Chloride of Ethyl.}} + \underbrace{(C_2\,H_5)_3\quad N}_{\text{Triethylamine.}}$$

$$\underbrace{[(C_2\,H_5)_3\,H\ N]\,Cl}_{\text{Chloride of Triethylammonium.}} = (C_2\,H_5)\,Cl + \underbrace{(C_2\,H_5)_2\,H\ N}_{\text{Diethylamine.}}$$

$$\underbrace{[(C_2\,H_5)_2\,H_2\,N]\,Cl}_{\text{Chloride of Diethylammonium.}} = (C_2\,H_5)\,Cl + \underbrace{(C_2\,H_5)\ H_2\,N}_{\text{Ethylamine.}}$$

$$\underbrace{[(C_2\,H_5)\ H_3\,N]\,Cl}_{\text{Chloride of Ethylammonium.}} = (C_2\,H_5)\,Cl + \underbrace{H_3\,N}_{\text{Ammonia.}}$$

The above reactions, interesting when regarded from a scientific point of view, admit of but limited application in practice. The purity of the result is disturbed by several circumstances, which it is difficult to exclude. Unless the temperature be sufficiently high, a small portion of the ammonium-salt submitted to distillation sublimes without change; again, a portion of the same salt is reproduced in the neck of the retort and in the receiver*, from the very constituents into which it splits; lastly, if the temperature be too high, the chloride of ethyl is apt to be decomposed into ethylene and hydrochloric acid, the latter producing, with the monamine liberated in the reaction, a salt which in its turn is likewise decomposed.

---

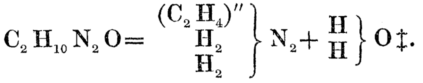
* This inconvenience may be partly obviated by distilling into an acid.

Thus the chloride of diethylammonium, for instance, together with chloride of ethyl and ethylamine, yields ethylene and chloride of ethylammonium which splits into chloride of ethyl and ammonia.

The idea naturally suggested itself, to attempt, by means of this reaction, the formation of the primary and secondary monophosphines, which are at present unknown. Experiments made with the view of transforming triethylphosphine into diethylphosphine have as yet remained unsuccessful, the chloride of triethylphosphonium distilling without alteration.

X. "Notes of Researches on the Polyammonias."—No. IX. Remarks on *anomalous* Vapour-densities. By A. W. HOFMANN, LL.D., F.R.S. Received July 24, 1860.

In a note addressed to the Royal Society[*] at the commencement of this year, I have shown that the molecules of the diamines, like those of all other well-examined compounds, correspond to two volumes of vapour[†], and I have endeavoured to explain the apparent anomalous vapour-densities of the hydrated diamines by assuming that the vapour-volume experimentally obtained was a mixture of the vapour of the anhydrous base and of the vapour of water. Thus, hydrated ethylene-diamine was assumed to split under the influence of heat into anhydrous ethylene-diamine (2 vols. of vapour) and water (2 vols. of vapour).



$$C_2H_{10}N_2O = \left.\begin{matrix}(C_2H_4)''\\ H_2\\ H_2\end{matrix}\right\}N_2 + \left.\begin{matrix}H\\ H\end{matrix}\right\}O\text{[‡]}.$$

The vapour-density of ethylene-diamine referred to hydrogen being 30, and that of water vapour 9, the vapour-density of a mixture of equal volumes of ethylene-diamine and water-vapour $= \frac{30+9}{2} = 19{\cdot}5$, which closely agrees with the result of experiment.

In continuing the study of the diamines, I have expanded these

---

[*] Proceedings, vol. x. p. 224.

[†] $H_2O = 2$ vols.

[‡] $H=1$; $O=16$; $C=12$, &c.